Regression analysis for the sorption isotherms of basic dyes on sugarcane dust

Yuh-Shan Ho a,*, Wen-Ta Chiu b, Chung-Chi Wang a

a School of Public Health, Taipei Medical University, 250 Wu-Hsing Street, Taipei 11014, Taiwan
b Taipei Medical University-Associated Wan-Fang Hospital, 111 Hsing-Long Road, Sec. 3, Taipei 116, Taiwan

Received 25 May 2004; received in revised form 12 October 2004; accepted 16 October 2004
Available online 20 January 2005

Abstract

The sorption of three basic dyes, named basic violet 10, basic violet 1, and basic green 4, from aqueous solutions onto sugarcane dust was studied. The results revealed the potential of sugarcane dust, a waste material, to be a low-cost sorbent. Equilibrium isotherms were analyzed using the Langmuir, the Freundlich, and the three-parameter Redlich–Peterson isotherms. In order to determine the best-fit isotherm for each system, two error analysis methods were used to evaluate the data: the linear coefficient of determination and the Chi-square statistic test for determination of a non-linear model. Results indicated that the Chi-square test provided a better determination for the three sets of experimental data.

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Keywords: Sugarcane; Adsorption; Biosorption; Isotherm; Basic dye; Chi-square; Alternative determination method

1. Introduction

Sorption techniques produce high-quality treated effluents, and sorption processes have been investigated as a method of removing pollutants from wastewaters. Due to it being a cheaper pollution control method, a membrane-media extraction, which uses peat moss “capsules” for effectively reducing concentrations of heavy metals from wastewater, has been developed and used in industry (Green et al., 1994). An accurate mathematical description of the equilibrium isotherms is essential to the effective design of sorption systems. In 1906, Freundlich presented an empirical sorption isotherm that can be used for non-ideal systems. The Freundlich isotherm is the earliest known relationship describing the sorption equation. In 1916, Langmuir developed a relationship between the amount of gas absorbed onto an adsorbent and the pressure of that gas.

Such equations are now referred to as Langmuir sorption isotherms, a theoretically based sorption isotherm in the ideal case. Jossens et al. (1978) modified the three-parameter isotherm proposed by Redlich and Peterson (1959) to incorporate features of both the Langmuir and Freundlich equations.

Three sorption isotherm models, the Langmuir, Freundlich, and Redlich–Peterson, have been widely applied, and linear regression has been used to determine the best-fitting model throughout the years. Using linear regression to determine the best-fitting model was not only an easier way at the time when it was first proposed, but also it has become a “custom” principle nowadays. The coefficient of determination, the sum of the errors squared, a hybrid error function (Marquardt’s percent standard deviation), the average relative error, and the sum of the absolute errors are used to evaluate isotherm data as non-linear methods (Ho et al., 2002; Allen et al., 2003; Ng et al., 2003; Ho, 2004).

A number of agricultural waste and by-products of cellulose origin have been studied in the literature for
their capacity to remove dyes from aqueous solutions, such as barley husks, sugarcane bagasse, wheat straw (Chandran et al., 2002), corn cobs, barley husks (Robinson et al., 2002), tree ferns (Ho et al., 2005), wood chips, and corn-cob shreds (Nigam et al., 2000). Several studies have also been performed using activated carbon prepared from agricultural wastes for the removal of dye from aqueous solutions. These include jackfruit peel, pearl millet husks (Inbaraj et al., 2002; Inbaraj and Sulochana, 2002), peanut hulls (Girgis et al., 2002), and coir pith (Namasiyavam and Kavitha, 2002). In addition, inexpensive and efficient cellulose-based adsorbents prepared by the reaction of cross-linked polyethyleneimine (CPEI) with wood sawdust have also been reported (Ibrahim et al., 1997).

In this paper, we attempt to use an agricultural by-product, sugarcane dust, as a sorbent. Sugarcane dust is a complex material basically containing lignin and cellulose as the major constituents (Abd-El-Thalouth et al., 1993). Cellulose can be a sorbent for removing dyes from solution (Youssef, 1993). A strong anion-exchange resin was prepared from sugarcane bagasse, a lignocellulosic byproduct of sugarcane processing, which effectively and inexpensively decolorizes dyehouse wastewater in an environmentally benign manner (Laszlo, 1996). Sugarcane bagasse has been studied for removing acid dyes such as acid red 114 and acid blue 25 (McKay et al., 1987), basic dyes such as basic red 22, basic blue 69 (McKay et al., 1987), malachite green, methylene blue, crystal violet, and rhodamine B (Khattari and Singh, 1999), direct dyes (Abd-El-Thalouth et al., 1993), and reactive dyes (Laszlo, 1996).

In this study, Chi-square test was used, and isotherm parameters were determined using the method of least squares. Two two-parameter equations, the Freundlich and Langmuir isotherms, and a three-parameter equation, the Redlich–Peterson isotherm, were utilized due to their ability to model equilibrium sorption data. Results of the linear and non-linear correlation analyses of these three isotherms were compared using the sorption of three basic dyes, namely basic violet 10, basic violet 1, and basic green 4 on sugarcane dust.

2. Methods

The raw sugarcane dust was obtained from a market as solid waste. The sugarcane dust was washed, dried at a temperature of 60 °C for 96 h, and then ground and finally screened to obtain a particle size range of 351–589 μm before use. The solutions of basic violet 10 (BV10), basic violet 1 (BV1), and basic green 4 (BG4) were prepared in deionized water. All solutions used in this study were diluted with deionized water as required.

Fifty milliliters of a dye solution at natural pH values with a proper range of concentrations (30–70 mg/dm³) for BV10, 150–250 mg/dm³ for BV1, and 60–130 mg/dm³ for BG4), and 0.25 g of an accurately weighed sugarcane dust sample were placed in a 125-ml conical flask. A series of such conical flasks was then shaken at a constant speed of 100 rpm in a 25 °C water bath for 24 h. Then the sugarcane dust was separated by centrifugation, and the solution was analyzed for the remaining dye concentration using a spectrophotometer at $\lambda_{\text{max}}$ of 556.5 nm for BV10, 583 nm for BV1, and 617 nm for BG4.

3. Equilibrium isotherms

Equilibrium isotherm equations are used to describe the experimental sorption data. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanisms and the surface properties and affinities of the sorbent. The three most common isotherms for describing solid–liquid sorption systems are the Langmuir, the Freundlich, and the Redlich-Peterson isotherms.

3.1. The Langmuir isotherm

The theoretical Langmuir isotherm (Langmuir, 1916) is often used to describe sorption of a solute from a liquid solution as

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}.$$  

(1)

The constants $q_m$ and $K_a$ are characteristics of the Langmuir equation and can be determined from a linearized form of Eq. (1), represented by

$$\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{1}{q_m}.$$  

(2)

A plot of $C_e/q_e$ versus $C_e$ should indicate a straight line of slope $1/q_m$ and an intercept of $1/(K_a q_m)$.

Alternatively

$$\frac{1}{q_e} = \left( \frac{1}{K_a q_m} \right) \frac{1}{C_e} + \frac{1}{q_m},$$  

(3)

which will have a straight line with a slope of $1/(K_a q_m)$ and an intercept of $1/q_m$ when $1/q_e$ is plotted against $1/C_e$, where $C_e$ is the equilibrium concentration (mg/dm³), $q_e$ the amount of dye sorbed (mg/g), $q_m$ is $q_e$ for a complete monolayer (mg/g), and $K_a$ is the sorption equilibrium constant (dm³/mg).

3.2. The Freundlich isotherm

The Freundlich isotherm (Freundlich, 1906) is the earliest known relationship describing the sorption equation. This fairly satisfactory empirical isotherm
can be used for non-ideal sorption that involves heterogeneous sorption and is expressed by the following equation:

\[ q_e = K_F C_1^n. \]  

(4)

The equation may be linearized by taking the logarithm of both sides

\[ \log(q_e) = 1/n \log(C_e) + \log(K_F), \]

(5)

which will have a straight line with a slope of \(1/n\) and an intercept of \(\log(K_F)\) when \(\log(q_e)\) is plotted against \(\log(C_e)\), where \(K_F\) and \(1/n\) are empirical constants dependent on several environmental factors.

3.3. The Redlich-Peterson isotherm

The Redlich–Peterson isotherm (Redlich and Peterson, 1959) contains three parameters and involves the features of both the Langmuir and the Freundlich isotherms. It can be described as follows:

\[ q_e = \frac{A C_e}{1 + B C_e^g}. \]

(6)

Then take the natural logarithm of both sides

\[ \ln \left( \frac{AC_e}{q_e} - 1 \right) = g \ln(C_e) + \ln(B). \]

(7)

Although a linear analysis is not possible for a three-parameter isotherm, three isotherm constants, \(A\), \(B\) and \(g\), can be evaluated from the pseudo-linear plot represented by Eq. (7) using a trial-and-error optimization method. A general trial-and-error procedure which is applicable to computer operations was developed to determine the coefficient of determination, \(r^2\) for a series of values of \(A\) for the linear regression of \(\ln[C_e/(C_e/q_e) - 1]\) and to obtain the best value of \(A\) which yields a maximum ‘optimized’ value of \(r^2\).

4. Error analysis

In the single-component isotherm studies, the optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the isotherm to the experimental equilibrium data. In this study, linear coefficients of determination and a non-linear Chi-square test were used.

The Chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models. The equivalent mathematical statement is

\[ \chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}}, \]

(8)

where \(q_{e,m}\) is the equilibrium capacity obtained by calculating from the model (mg/g), and \(q_e\) is experimental data of the equilibrium capacity (mg/g). If data from the model are similar to the experimental data, \(\chi^2\) will be a small number; if they are different, \(\chi^2\) will be a large number. Therefore, it is necessary to also analyze the data set using the Chi-square test to confirm the best-fit isotherm for the sorption system.

5. Results and discussion

The simplest method to determine isotherm constants for two-parameter isotherms is to transform the isotherm variables, so that the equation is converted to a linear form and then to apply the linear regression.

5.1. The Langmuir isotherm

Typically, the sorption data were analyzed according to the linear form of the Langmuir isotherm (Eq. (2)). Plots of the specific sorption, \(C_e/q_e\) against the equilibrium concentration, \(C_e\) for BV10, BV1, and BG4 are shown in Fig. 1, and the linear isotherm constants \(q_m\) and \(K_a\) and the coefficient of determination, \(r^2\) are presented in Table 1. These isotherms were found to be linear over the entire concentration range studied with extremely high \(r^2\) values. The \(r^2\) values suggest that the Langmuir isotherm provides a good model of the sorption system. The sorption constant, \(K_a\) and the saturated monolayer sorption capacity, \(q_m\) for BV1 were higher than those for BV10 and BG4. Alternatively, Fig. 2 shows experimental data and the linear form of the
Langmuir isotherm (Eq. (3)). The linear isotherm constants, $q_m$, $K_a$ and $r^2$ are also listed in Table 1. The individual constants, $K_a$ and $r^2$ significantly differ, although the ratios give values for the monolayer saturation capacity, $q_m$ which are very close to those obtained using Eqs. (2) and (3). In Table 2, a comparison of values of the Langmuir monolayer saturation capacity, $q_m$ is made for the sorption of basic dyes onto various substances.

5.2. The Freundlich isotherm

The Freundlich isotherm plots for the sorption of the three basic dyes on sugarcane dust are presented in Fig. 3. Examination of the plot suggests that the linear Freundlich isotherm is also a good model for the sorption of basic dyes. Table 1 shows the linear Freundlich sorption isotherm constants, $K_F$ and $1/n$, and the coefficients of determination, $r^2$. Based on the $r^2$ values, the linear form of the Freundlich isotherm appears to produce a reasonable model for sorption in all three systems, with the BV1 and BG4 isotherms seemingly better fits of the experimental data than BV10.

5.3. The Redlich–Peterson isotherm

The Redlich–Peterson isotherm plots for sorption of the three basic dyes on sugarcane dust are presented in Fig. 4. Again, examination of the plot shows that the Redlich–Peterson isotherm accurately describes the sorption behaviors of BV10, BV1, and BG4 on sugarcane dust over the concentration ranges studied. The Redlich–Peterson isotherm constants, $A$, $B$, $g$, and $r^2$ are presented in Table 1. Since the method used to derive the isotherm parameters maximizes the linear coefficient of determination, it is unsurprising that in all cases, the Redlich–Peterson isotherms exhibit extremely high $r^2$ values indicating, superficially at least, that it produces a considerably better fit compared to the preceding two-parameter isotherms. In the case of BG4, $r^2$ for the two linear forms of Langmuir isotherm Eqs. (2) and (3) significantly differed. If just the linear form of Eq. (2) is used, the Redlich–Peterson isotherm was the most-suitable isotherm for the data followed by the Langmuir and then Freundlich isotherm. On the other hand, if the linear form of Eq. (3) is used, the Redlich–Peterson isotherm was still the most-suitable isotherm, followed by the Freundlich then the Langmuir isotherm. Even though the most-suitable isotherm for the data set was the Redlich–Peterson isotherm, the difference between the two linear forms of the Langmuir

Table 1
Comparison of linear regression coefficients of determination, $r^2$ and isotherm parameters

<table>
<thead>
<tr>
<th>Dye</th>
<th>Langmuir (Eq. (2))</th>
<th>Langmuir (Eq. (3))</th>
<th>Freundlich (Eq. (5))</th>
<th>Redlich–Peterson (Eq. (7))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r^2$</td>
<td>$q_m$</td>
<td>$K_a$</td>
<td>$r^2$</td>
</tr>
<tr>
<td>BV1</td>
<td>0.998</td>
<td>50.4</td>
<td>0.802</td>
<td>0.966</td>
</tr>
<tr>
<td>BV10</td>
<td>0.993</td>
<td>13.9</td>
<td>0.473</td>
<td>0.930</td>
</tr>
<tr>
<td>BG4</td>
<td>0.995</td>
<td>20.6</td>
<td>0.111</td>
<td>0.983</td>
</tr>
</tbody>
</table>

Table 2
Comparison of non-linear regression coefficients of determination, $r^2$ and the Chi-square test statistic $\chi^2$

<table>
<thead>
<tr>
<th>Dye</th>
<th>L-1 $r^2$</th>
<th>L-2 $r^2$</th>
<th>Freundlich (Eq. (6)) $r^2$</th>
<th>Redlich–Peterson (Eq. (4)) $r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BV1</td>
<td>0.720</td>
<td>0.968</td>
<td>0.204</td>
<td>0.960</td>
</tr>
<tr>
<td>BV10</td>
<td>0.174</td>
<td>0.948</td>
<td>0.199</td>
<td>0.949</td>
</tr>
<tr>
<td>BG4</td>
<td>0.0895</td>
<td>0.978</td>
<td>0.0799</td>
<td>0.970</td>
</tr>
</tbody>
</table>

L-1, Langmuir-1 (Eq. (1)), $q_m$ and $K_a$ obtained from Eq. (2).
L-2, Langmuir-2 (Eq. (1)), $q_m$ and $K_a$ obtained from Eq. (3).
isotherms significantly affected the result. This denotes that a different axis setting would alter the results of the linear regression and hence influence the determination process.

5.4. Non-linear analysis

The Chi-square statistic, $\chi^2$, and coefficient of determination, $r^2$ were obtained and are shown in Table 3. In the non-linear analysis, $\chi^2$ of the Langmuir isotherms whose constants were obtained from the two different linear forms of the Langmuir isotherms were almost identical. The Redlich–Peterson and Freundlich isotherms exhibited lower $\chi^2$ values than the Langmuir, which was considered to be a better fit compared to the Langmuir isotherm. Fig. 5 shows the isotherm plots and the experimental data. Langmuir isotherms whose constants were obtained from Eqs. (2) and (3) respectively, the Freundlich isotherm, and the Redlich–Peterson isotherm. Therefore, drawing conclusions from the non-linear Chi-square analysis, the Redlich–Peterson isotherm was the best-fitting isotherm, followed by the Freundlich model for this sorption system. Unlike the linear analysis, different forms of the equation affected $r^2$ values less significantly. Therefore, the non-linear Chi-square analysis might be a method of avoiding such errors.

5.5. Linear versus non-linear

Under the basic condition of the BG4 sorption system, it was estimated to be more likely to approach...
the Freundlich form: this can be seen from the data that the values of g approached 0.818 (<1). However, linear regression and the non-linear Chi-square analysis gave different models as the best-fitting isotherm for the given data set, thus indicating a significant difference between the analytical methods. As most of the chemical analysis still mostly relied on linear regression due to its simplicity compared to the non-linear Chi-square analysis, this may have led to an inaccurate conclusion. Therefore, it is suggested that the data set be evaluated by both linear and non-linear regression analyses to ensure better results. In addition, non-linear optimization techniques were reported earlier (Seidel and Gelbin, 1988) to determine isotherm parameters. Currently, non-linear error functions have also been examined, and the isotherm parameters were determined by minimizing the error function using the solver add-in with Microsoft’s spreadsheet, Excel (Microsoft) (Ho et al., 2002; Allen et al., 2003; Ng et al., 2003). A non-linear Chi-square analysis was also reported in the sorption of cadmium from solution by tree fern (Ho, 2004).

6. Conclusions

The results revealed the potential of sugarcane dust, a waste material, to be a low-cost sorbent for removing basic dyes. The Langmuir monolayer saturation sorption capacities for the three basic dyes were 50.4, 20.6, and 13.9 mg/g sugarcane dust for basic violet 1, basic green 4, and basic violet 10, respectively. The best-fitting isotherm parameters were determined by minimizing the error function using the solver add-in with Microsoft’s spreadsheet, Excel (Microsoft) (Ho et al., 2002; Allen et al., 2003; Ng et al., 2003). A non-linear Chi-square analysis was also reported in the sorption of cadmium from solution by tree fern (Ho, 2004).

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